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NSWC TR 86-390

SAFETY EVALUATION OF THE EXPENDABLE SOUND VELOCITY PROBE (SSXSV)

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The Arctic Submarine Laboratory, Naval Ocean Systems Center, San Diego, sought approval to carry the Expendable Sound Velocity Probe (SSXSV) on board submarines. The battery used by the SSXSV employs a lithium/manganese dioxide couple. The battery is assembled by the SSXSV supplier - Sippican Ocean Systems, Inc. - from a Duracell PX28L battery and a $DL\frac{1}{3}N$ cell. The Naval Surface Weapons Center, White Oak, conducted a safety evaluation of the SSXSV as required by NAVSEA Notice 9310. This report presents the results of the safety evaluation of the SSXSV.

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FOREWORD

This work presents the results of the safety evaluation performed on the Expendable Sound Velocity Probe. The evaluation was initiated by the Arctic Submarine Laboratory, Naval Ocean Systems Center, San Diego. The purpose of the evaluation was to obtain approval for internal carriage of the probe unit on board submarines. The safety evaluation performed on the system was conducted in accordance with NAVSEA Notice 9310 by the Naval Surface Weapons Center, White Oak.

Approved by:

W. T. MESSICK, Acting Head
Materials Division

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CHAPTER 1

INTRODUCTION

The Expendable Sound Velocity Probe (SSXSV) is manufactured by Sippican Ocean Systems, Inc. The SSXSV battery is manufactured by Duracell International, Inc.

The SSXSV probe pictured in Figure 1 consists of a small probe and a monitoring lead spool (for transmitting sound data to the submarine), encased in a metal launch canister. The canister is 98cm in length and 7.5cm in diameter. The portion of the canister which contains the probe and battery is sealed, isolating the probe and battery from the outside atmosphere. The battery being used employs a lithium/manganese dioxide (Li/MnO_2) couple, comprised of three 3-volt (V) cells. The single cells are Duracell DL$\frac{1}{3}$N cells. The anode, cathode, and total cell reactions are given by equations 1, 2, and 3, respectively. Two of the DL$\frac{1}{3}$N cells

$$Li \longrightarrow Li^{+} + e^{-} \tag{1}$$

$$Mn^{IV}O_2 + Li^{+} + e^{-} \longrightarrow Mn^{III}O_2(Li^{+}) \tag{2}$$

$$Li + Mn^{IV}O_2 \longrightarrow Mn^{III}O_2(Li^{+}) \tag{3}$$

are connected in series and encased in a metal can by Duracell to make a commercially available PX28L battery. The third cell is then connected in series with the PX28L by Sippican to give a nominal battery voltage of 9V. The capacity (C) for this battery is rated by the manufacturer at 160 milliampere•hours (mAh) at a rate of C/30.

The safety evaluation was performed by the Naval Surface Weapons Center. White Oak (NSWC/WC), on the SSXSV system containing the Duracell battery. Preliminary experiments were also run on the battery alone. The evaluation was conducted in accordance with procedures outlined by NAVSEA Notice 9310.

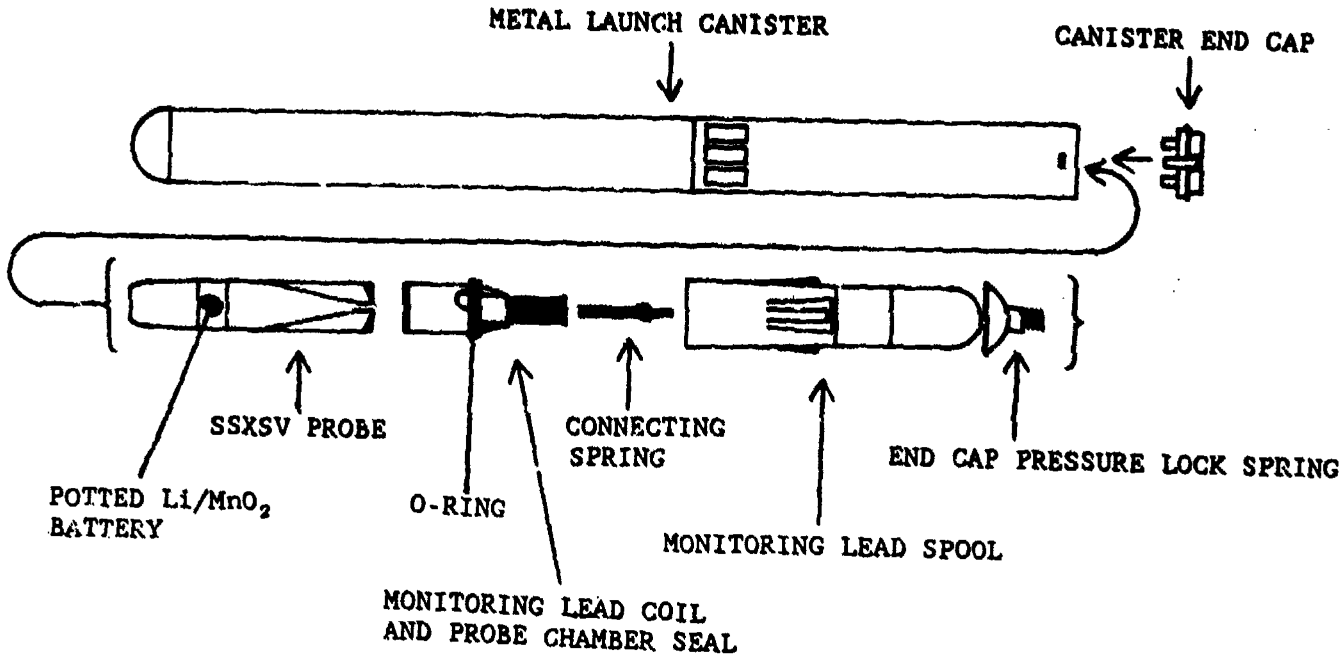

FIGURE 1. SSXSV PROBE/CANISTER CONFIGURATION

CHAPTER 2

EXPERIMENTAL

DL$\frac{1}{3}$N cells and PX28L batteries were obtained by NSWC from Duracell International, Inc., for testing. The lot of DL$\frac{1}{3}$N cells studied was labeled 500084-1 and the lot of PX28L batteries was labeled 500085-1. Seven SSXSV probes (lot label UISSXSV 300648-1), sent to NSWC by Sippican for testing, were sequentially numbered from 13973 to 13979. Eighteen batteries, independent of probe units, and seven batteries potted in probe units were tested. Six SSXSV batteries were shorted; six SSXSV batteries were discharged at a constant current and forced into voltage reversal; two PX28L batteries were heated; three SSXSV batteries were discharged, followed by charging; and one fresh SSXSV battery was charged. Batteries in three of the SSXSV probes were shorted and batteries in four of the probes were discharged at a constant current and forced into voltage reversal.

BATTERY TESTING

All batteries except those which were heated to high temperatures, were wrapped with glass tape and FIBERFRAX insulation to simulate the heat retention in the SSXSV system.

Short Circuit Testing

One DL$\frac{1}{3}$N Li/MnO_2 cell was connected in series with one PX28L Li/MnO_2 battery (two DL$\frac{1}{3}$N cells connected in series and encased in a metal can) to produce a 9V SSXSV battery. Six of these batteries were prepared by the staff of NSWC/WO and then shorted through less than .02 ohm (Ω). The battery current and voltage were monitored and the temperatures of the PX28L can (thermocouple no. 1) and the DL$\frac{1}{3}$N can (thermocouple no. 2) were also monitored. Five of the batteries were shorted for approximately two hours and one battery was shorted for 16 hours.

Constant Current Discharge and Reversal Testing

Six three-cell batteries, prepared as before, were discharged through 112Ω at the C/2 rate (80mA rate). When the voltage dropped to 0 volt, the battery was driven 150 percent into voltage reversal using an external power supply with current limited to 100 mA and voltage limited to 20V. The voltage and current of the batteries were monitored along with the can temperatures of the PX28L (thermocouple no. 1) and the DL$\frac{1}{3}$N (thermocouple no. 2).

High Temperature Testing

Two PX28L batteries were wrapped with THERMOLYNE BRISKHEAT flexible electric heating tape. These batteries were then heated (at a rate of 20°C/minute) until the heating tape failed. The voltage and can temperature of the batteries were monitored.

Charging Discharged Batteries

Three SSXSV batteries were discharged and then charged. One of the three SSXSV batteries was discharged 50 percent of the advertised capacity through a 900Ω resistor at the 10mA rate. The battery was then charged (after incubating overnight) at the 100mA rate - voltage being limited to 20V - to 100 percent of the theoretical capacity. Two of the three SSXSV batteries were discharged 80 percent of the manufacturer's rated capacity through a 900Ω resistor at the 10mA rate. After incubating overnight, the batteries were charged at the 100mA rate to 100 percent of the theoretical capacity. The voltage, current, and can temperatures of the PX28L (thermocouple no. 1) and DL$\frac{1}{3}$N (thermocouple no. 2) were monitored.

Charging a Fresh Battery

One fresh SSXSV battery was charged at the 100mA rate for approximately four hours. The voltage, current, and can temperatures of the PX28L (thermocouple no. 1) and DL$\frac{1}{3}$N (thermocouple no. 2) were monitored.

SSXSV SYSTEM TESTING

All SSXSV batteries are potted inside a probe using a low stress epoxy encapsulation product (product no. SY6024) manufactured by Anchor Seal Epoxy Products.

Short Circuit Testing

Three batteries were shorted through less than .02Ω inside SSXSV probes. The voltage, current, and two thermocouples were monitored on each probe. For the first battery, a thermocouple was placed on the canister and a thermocouple was placed just inside the canister (where the voltage leads protruded through a plastic sealing cap). For the next two batteries tested, the placement of the thermocouples was changed. The probes were removed from the canisters and one thermocouple was placed just over the battery on the battery potting - the location of the battery was found using a magnet. The second thermocouple was placed in the nose hole of the probe. Figure 2 shows the placement of the thermocouples on the probe.

Constant Current Discharge and Reversal Testing

The batteries in the remaining four probes were discharged at the C/2 rate (80mA rate) through 112Ω and forced into voltage reversal with a power supply.

The first battery was discharged and forced into voltage reversal with the probe being outside the canister so the thermocouples could be easily positioned. The battery potting was found to be cracked when the probe was removed from the canister. Although this condition existed, the nominal voltage of the battery was normal (9.8V), and the test was conducted. The second probe battery was discharged and forced into voltage reversal in the same manner as the first but the potting was not cracked prior to testing. In order to trap venting gases and test the durability of the canister, the last two probes were discharged and forced into voltage reversal inside the canister. Holes were drilled and tapped in two canisters for a $\frac{1}{4}$-inch NPT pipe fitting. An evacuated stainless steel vessel was connected to this fitting to collect venting products. Thermocouples were placed on the outside of the canister and monitored along with voltage and current.

All voltage, current, and temperature readings were monitored and stored using an IBM PC/XT and a KEITHLEY data acquisition system. Some important events were also recorded on videotapes which are on file at NSWC/WO.

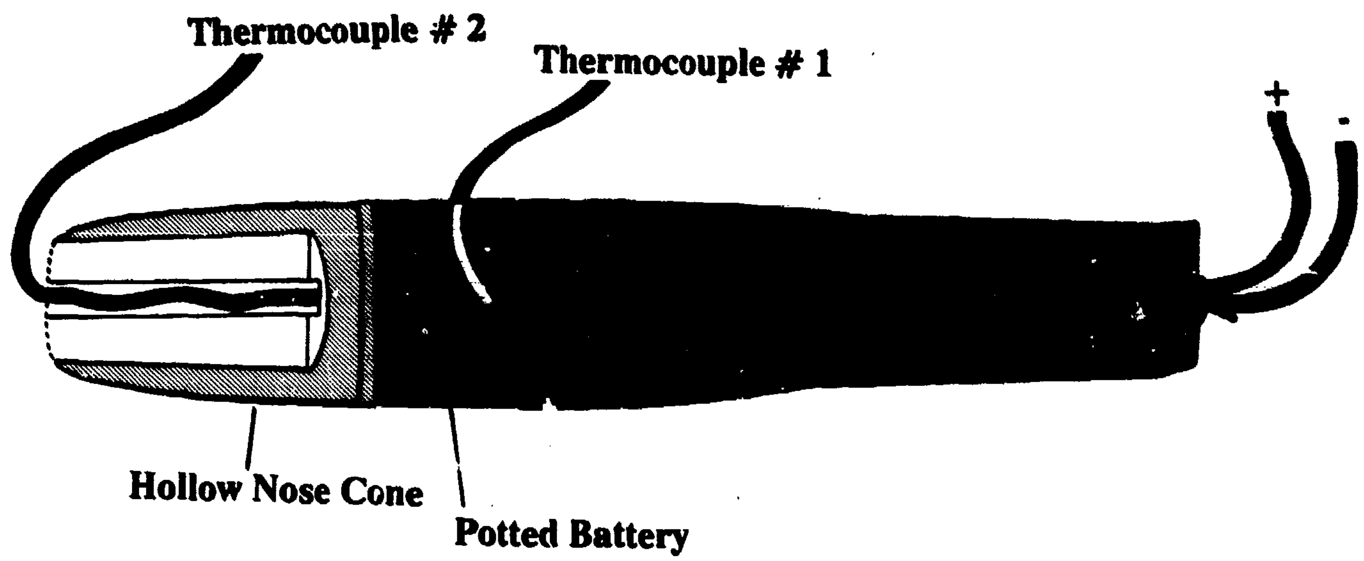

FIGURE 2. SSXSV PROBE THERMOCOUPLE PLACEMENT

CHAPTER 3

RESULTS AND DISCUSSION

BATTERY TESTING

Short Circuit Testing

Six SSXSV batteries (one $DL\frac{1}{3}N$ cell in series with one PX28L battery) were shorted. In less than five minutes voltage readings fell from 9.8 volt to 0 volt. Figure 3 is a representative graph of the short circuit tests. Note that within 30 minutes the temperature measured on the PX28L battery rose to a peak. On the average the peak temperature was 92°C. This temperature fell to ambient over a time period of about eight hours. The temperature measured on the single $DL\frac{1}{3}N$ cell, however, remained ambient throughout the test. The SSXSV battery did not explode, vent, leak electrolyto, or show any signs of disfiguration due to shorting.

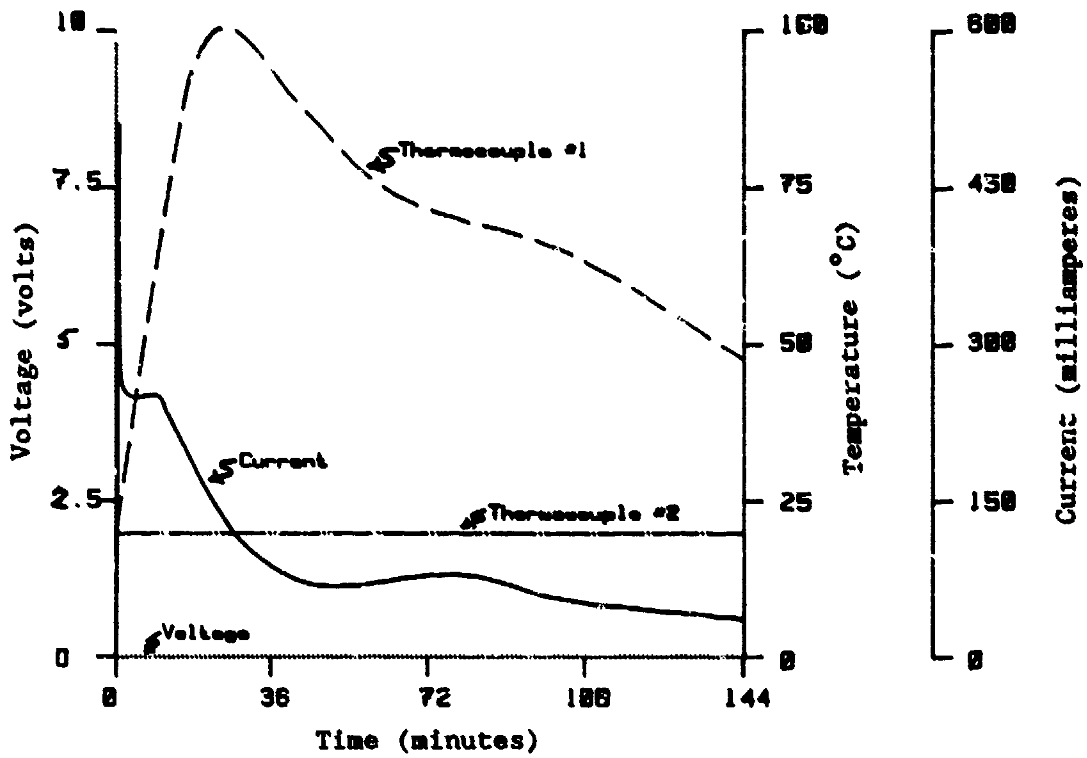

FIGURE 3. SHORT CIRCUIT OF AN SSXSV BATTERY NOT POTTED IN A PROBE

Constant Current Discharge and Reversal Testing

Six SSXSV batteries were discharged at a constant current and forced into voltage reversal with a power supply. The batteries were discharged at the 80mA rate to 0 volt and then additionally driven 150 percent into voltage reversal at the same current. The voltage continued to drop and by the end of the test reached approximately -10V. During the first 75 minutes of the test, the voltage dropped markedly (on the order of 10V) and then leveled off for 65 minutes. During the last portion of the test, the voltage again dropped. During this period the current also dropped (Figure 4). The average maximum temperature recorded on a forced overdischarge was 57°C. This maximum temperature was again recorded on the PX28L and the DL$\frac{1}{3}$N cell can temperature remained ambient. Like the batteries that were shorted, the batteries discharged into reversal did not explode, vent, leak electrolyte, or show any signs of disfiguration.

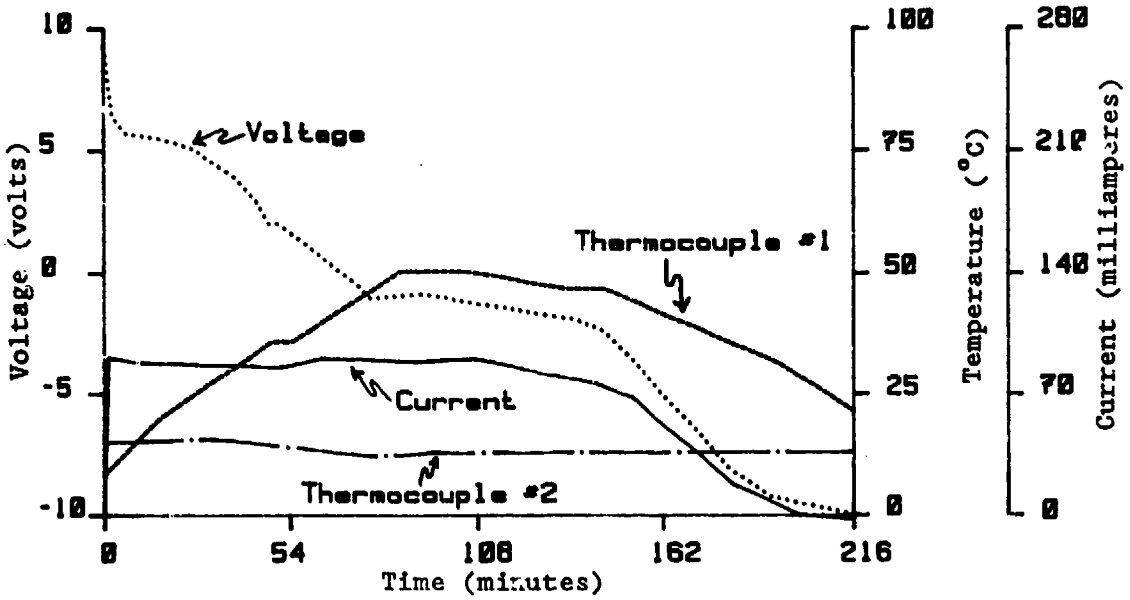

FIGURE 4. CONSTANT CURRENT DISCHARGE AND REVERSAL OF AN SSXSV BATTERY NOT POTTED IN A PROBE

High Temperature Testing

Two PX28L batteries were heated; at temperatures above 200°C, the negative ends of the batteries vented and severed the heat tape. A few minutes prior to the batteries venting, the open circuit voltage (OCV) faltered and began to drop. Figure 5 is a representative graph of a high temperature test conducted on a PX28L battery. The maximum temperatures recorded were 350°C and 435°C at the moment when failure occurred. Each cell in the battery failed at approximately the same time (differING by less than five seconds). The first cell failure occurred when the temperature maximum occurred. There was a small amount of burning (flames lasting less than ten seconds) associated with the failure of each battery.

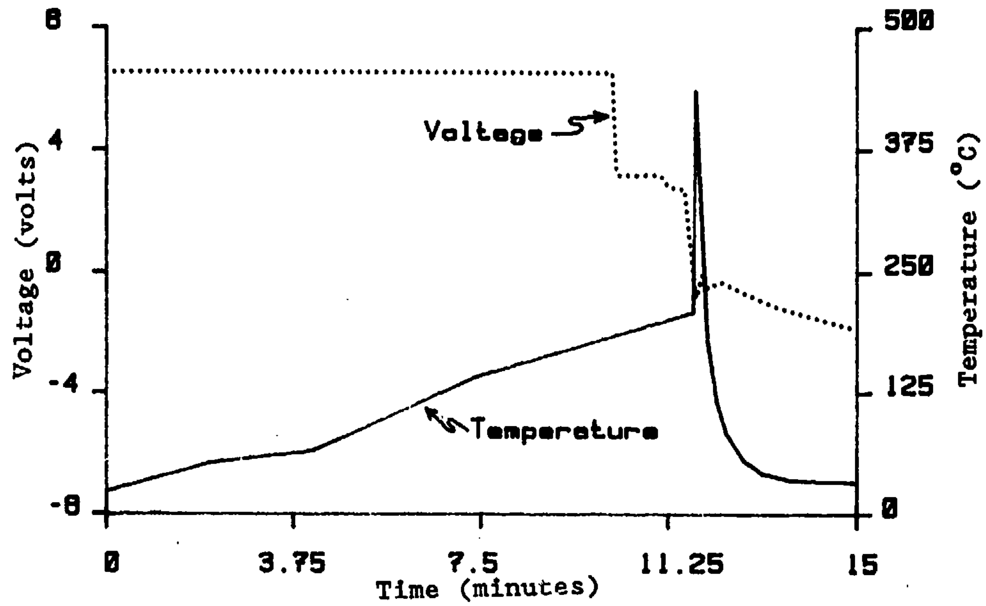

FIGURE 5. RESULTS OF HEATING A PX28L BATTERY

Charging Discharged Batteries

Three SSXSV batteries were discharged at the 10mA rate and then charged at the 100mA rate. The first battery was discharged 50 percent. During the discharge, the temperature on the PX28L and the $DL\frac{1}{3}N$ rose less than 5°C. During charging, the temperature on the $DL\frac{1}{3}N$ remained ambient but the temperature of the PX28L rose to 84°C. However, there was no explosion, venting, leakage of the electrolyte, or any signs of disfiguration. Figures 6 and 7 show the discharge and charging curves for this battery. The next battery was discharged at the 10mA rate to remove 80 percent of the capacity. The discharge took place over a period of two days and the temperatures measured on the PX28L and the $DL\frac{1}{3}N$ remained ambient. Figures 8 and 9 show the discharge curves for day one and two, respectively. Following discharge, the battery was charged at a current of 100mA. Thirty minutes into the charge, the battery vented. Small flames were observed which lasted about five seconds. From the beginning of the test, the temperature on the PX28L increased but the $DL\frac{1}{3}N$ temperature remained at ambient. It was the $DL\frac{1}{3}N$ that had ruptured even though its temperature was the one that remained at ambient. The temperature on the PX28L peaked at 108°C. The flames associated with the rupture burned in the area where the thermocouple was located on the single cell. For this reason it was deduced that thermocouple no. 2 was not working properly, which gave false ambient readings on the $DL\frac{1}{3}N$ cell. The current for this test started at 100mA as planned but unexpectedly increased to 220mA at the time of and just before the rupture. Figure 10 is a summary of this data. Another SSXSV battery was tested in the same manner to try and reproduce the results obtained in the previous charging. The results, however, were not the same; during charging the

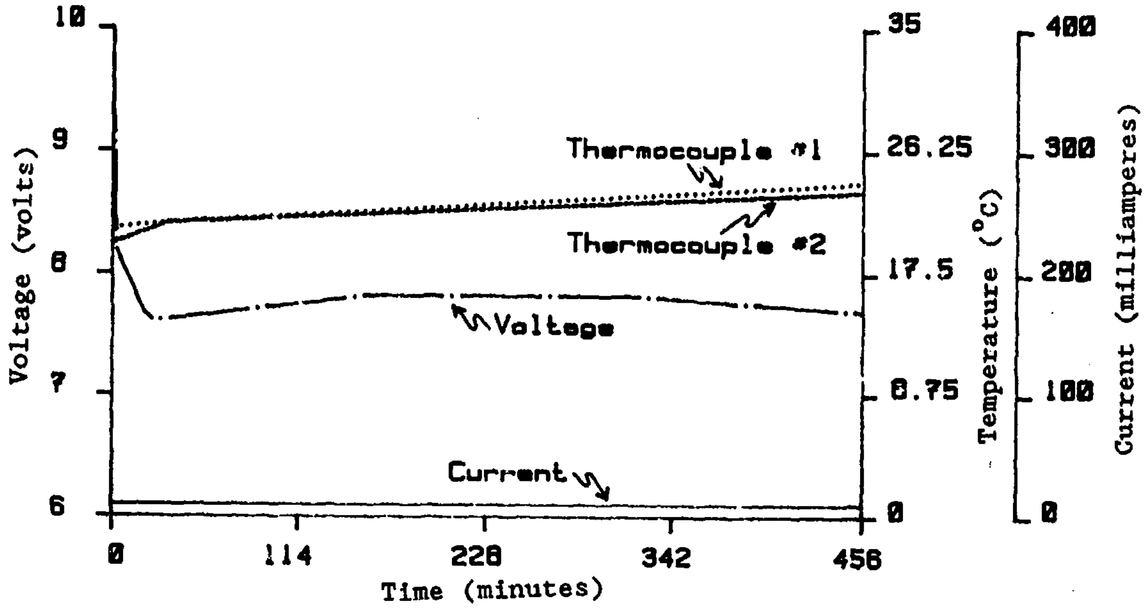

FIGURE 6. 10mA DISCHARGE OF AN SSXSV BATTERY (NOT POTTED IN A PROBE) TO 50% OF THE ORIGINAL CAPACITY

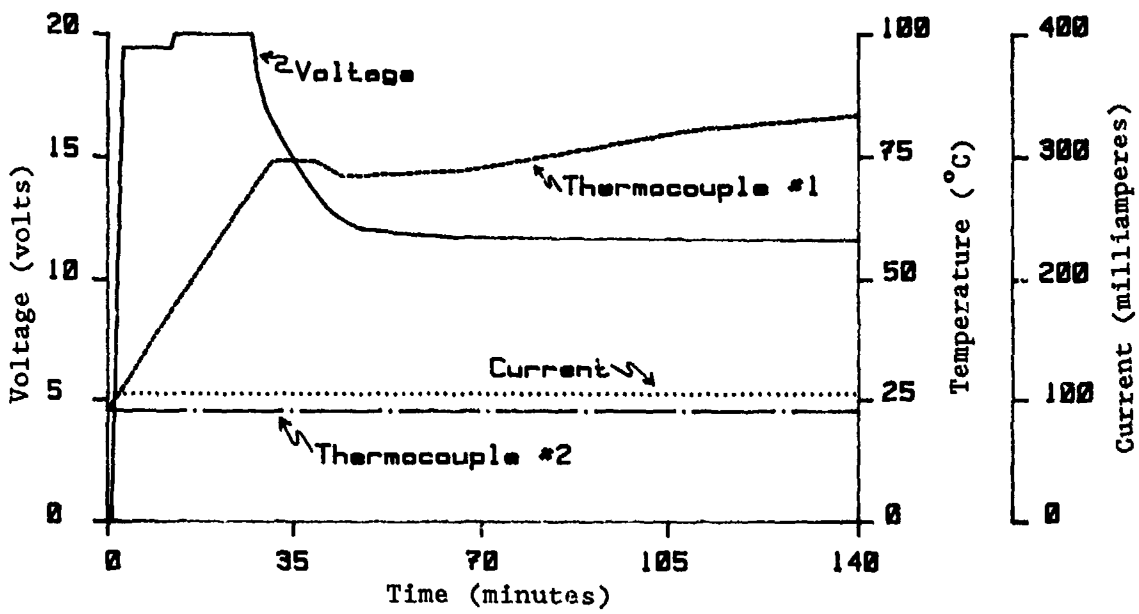

FIGURE 7. 100mA CHARGE OF A 50% DISCHARGED SSXSV BATTERY NOT POTTED IN A PROBE

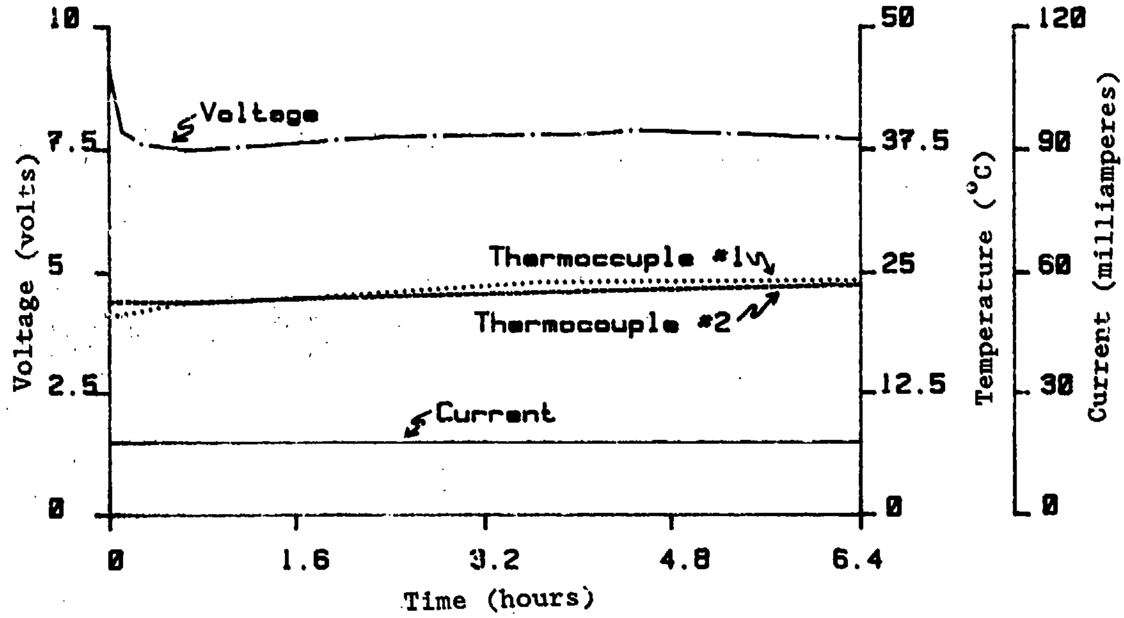

FIGURE 8. DAY 1 OF A 10mA DISCHARGE OF AN SSXSV BATTERY (NOT POTTED IN A PROBE) TO 80% CAPACITY REMOVAL

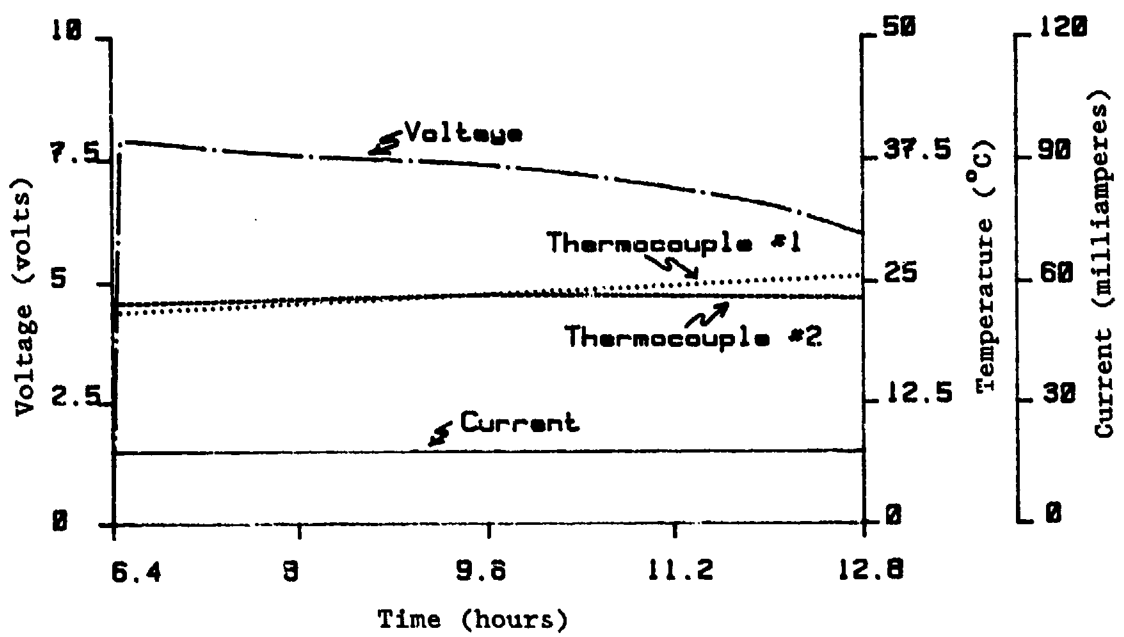

FIGURE 9. DAY 2 OF A 10mA DISCHARGE OF AN SSXSV BATTERY (NOT POTTED IN A PROBE) TO 80% CAPACITY REMOVAL

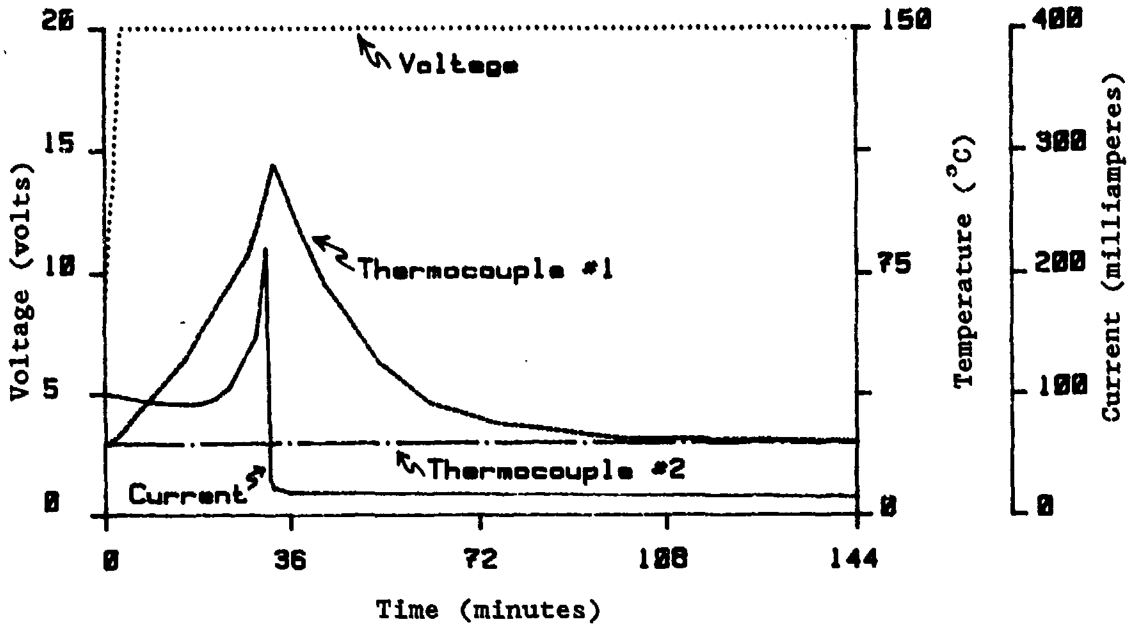

FIGURE 10. CHARGING DATA FOR ONE 80% PREVIOUSLY DISCHARGED SSXSV BATTERY NOT POTTED IN A PROBE

temperature of the PX28L rose to 82°C after 30 minutes and remained elevated. The temperature on the DL$\frac{1}{3}$N remained at ambient. After 30 minutes, the voltage dropped and the current remained relatively constant throughout the test. Figure 11 summarizes the charging data of this SSXSV battery.

Charging a Fresh Battery

One SSXSV battery was charged at the 100mA rate for four hours. All the pertinent data was recorded within the first 90 minutes of the test, and after 96 minutes the graphed data showed no change. Figure 12 shows the first 96 minutes of testing for this battery. The charging current was approximately 100mA initially. Forty minutes into the test, the power supply voltage automatically increased in response to a reduction in current caused by an apparent increase in battery impedance. The voltage reached the upper limit of the power supply at 20V. During this time, the temperature on the PX28L had peaked at 105°C. When the current had dropped to about 40mA the temperature began dropping. The DL$\frac{1}{3}$N temperature remained ambient and there was no explosion, venting, or leakage of electrolyte. However, both the PX28L and the DL$\frac{1}{3}$N showed signs of swelling.

SSXSV SYSTEM TESTING

Short Circuit Testing

Three SSXSV batteries, potted in three SSXSV probes, were shorted. Probe 1 (serial no. 13973) was shorted inside the SSXSV canister. The discharge curve

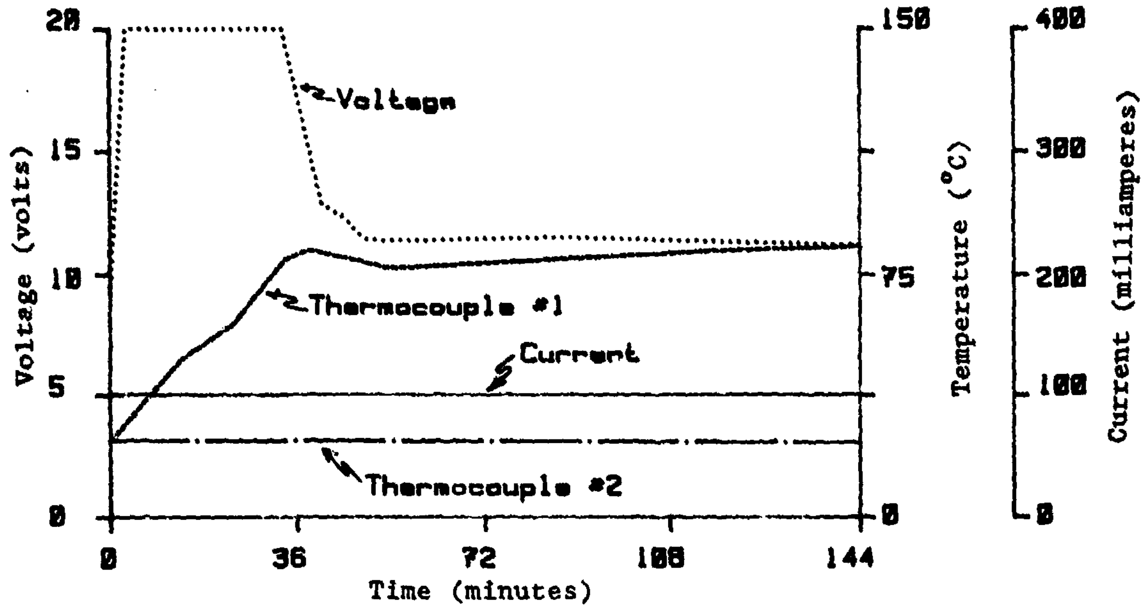

FIGURE 11. NORMAL CHARGING DATA OF AN 80% PREVIOUSLY DISCHARGED SSXSV BATTERY NOT POTTED IN A PROBE

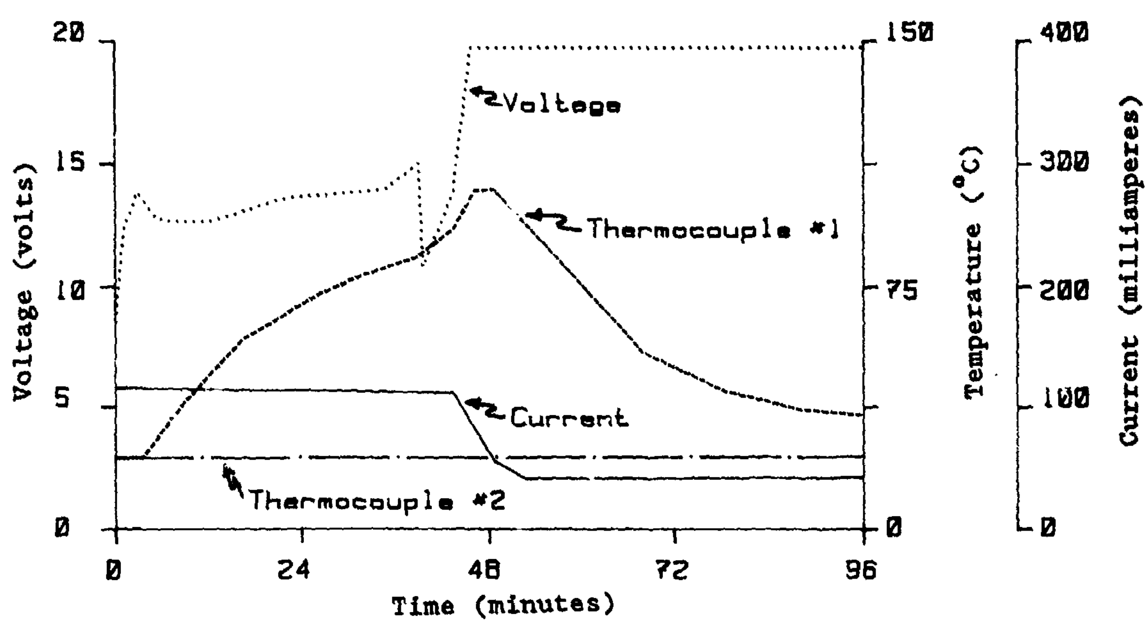

FIGURE 12. DATA FOR THE FIRST 96 MINUTES OF CHARGING A FRESH SSXSV BATTERY NOT POTTED IN A PROBE

resembled the discharge curves of the SSXSV batteries previously shorted. The temperatures monitored, however, were recorded as ambient. The thermocouples had been placed on the exterior of the canister; for the next two short circuit tests, the batteries (in probes) were tested outside the canister. Temperatures of the battery potting were monitored on the next two probes. The discharge curves for probe 2 (serial no. 13974) and probe 3 (serial no. 13975) were similar to the discharge curve for probe 1 in all respects except temperature. The average maximum temperature recorded on the potting of the two probes was 35°C, about 10°C above ambient. Figure 13 is a representative graph of shorting SSXSV batteries potted in probes. During these three tests, there were no ventings, explosions, leakage of electrolyte, or noticeable disfigurations associated with the probes. Dissection of the probes also disclosed that the batteries had not vented, exploded, leaked electrolyte, or become disfigured.

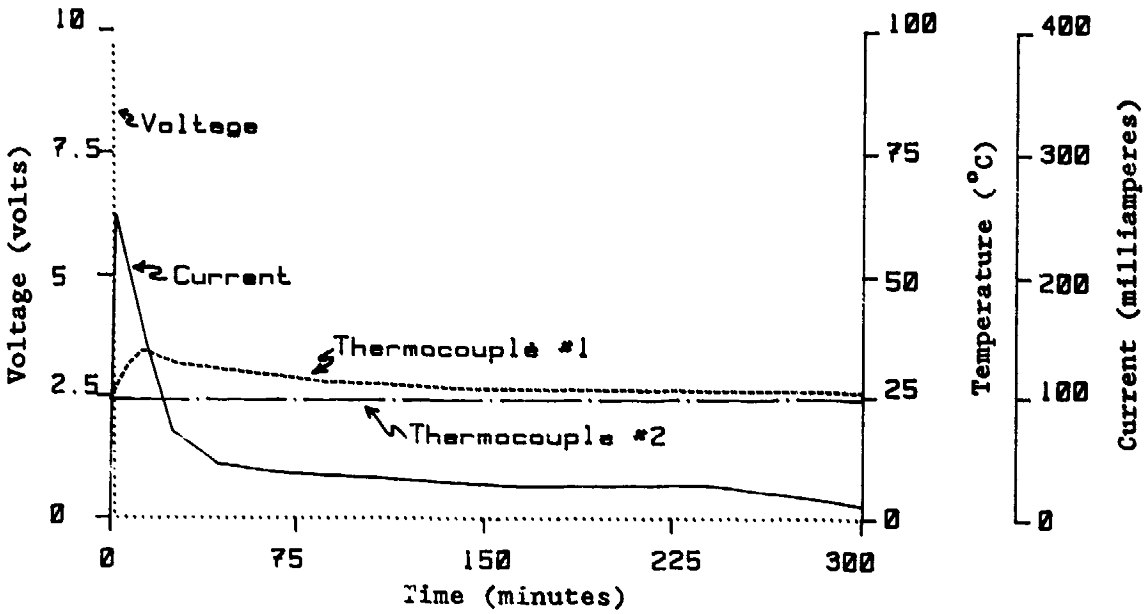

FIGURE 13. SHORT CIRCUIT DATA FOR AN SSXSV BATTERY POTTED IN A PROBE

Constant Current Discharge and Reversal Testing

Probe 4 (serial no. 13976), the first of four probes discharged into voltage reversal, had a crack in the battery potting prior to testing. The OCV of the battery was measured as 9.82V. Other OCV's for previous batteries tested were between 9V and 10V, so it was decided to proceed with the testing of this probe battery. No cause for the cracked potting was evident. The battery followed a normal discharge, reaching 0 volt, and then went into voltage reversal. After 2.5 hours of forced overdischarging, there was a venting (indicated by a "pop") accompanied by the tail piece cracking almost its entire length around the area where the potting was previously cracked. Three minutes later another venting occurred (also indicated by a "pop"). When the ventings occurred there was a noticeable smell, similar to the odor of ether. This probe was dissected. From

the arrangement of the cell, the battery, and the position of the crack it was not possible to say if thermal expansions, venting, or internal heat from either the PX28L or the DL$\frac{1}{3}$N caused the cracking. Testing performed on probe 5 (serial no. 13977) was similar to that of probe 4. The results were the same. About 2.5 hours into voltage reversal a venting occurred. The highest temperature seen for either probe was 51°C at the time of venting. Dissection of probe 5 revealed that thermal expansions in the DL$\frac{1}{3}$N and the proximity of this cell to the edge of the potting was the most probable cause of the cracking. Figure 14 is a representative graph for discharging an SSXSV battery (potted in a probe) into voltage reversal.

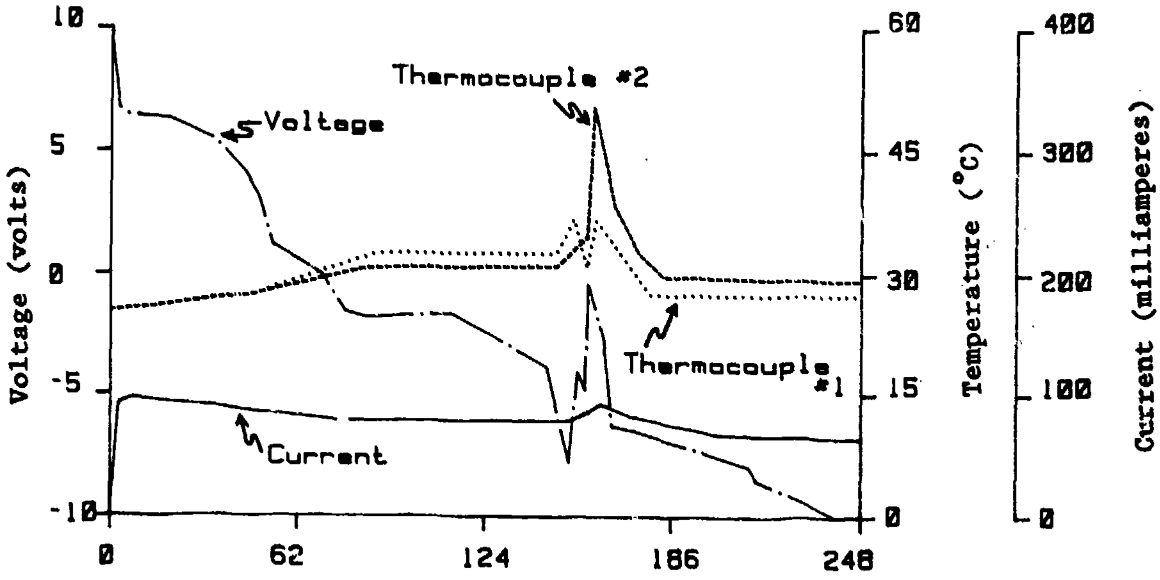

FIGURE 14. FORCED OVERDISCHARGE OF AN SSXSV BATTERY (POTTED IN A PROBE) AT THE C/2 RATE

Probe 6 (serial no. 13978) and probe 7 (serial no. 13979) were discharged into voltage reversal within the SSXSV canisters. The canister of probe 6 was pressure tested by filling it with oxygen (O_2) to 8 psi. After confirming that the canister was indeed a sealed environment, it was fitted with a gas collection vessel. About 2.5 hours into the discharge (the battery was into reversal at this time) venting occurred with a flame exiting the tube around the o-ring seal. However, this test was judged to be invalid as a test of canister durability. Apparently, a greater amount of O_2 than normal was trapped inside the canister, causing this reaction. If this were true, the gas sample collected from this canister would be expected to contain more O_2 than a sample collected from a canister in which the battery vented under normal conditions. Indeed, mass spectrometric analysis of off-gas products, performed by the National Bureau of Standards (project no. 5533462), revealed that this was the case. Probe 7 was also tested in the same manner as probe 6, with the exception that O_2 was not used to check canister sealing integrity. Probe 7 did not vent during discharge into voltage reversal at the 80mA rate, so 1 ampere (A) was driven through the battery by 100V which caused a mild venting. This allowed a gas sample to be collected. The off-gas products of probe 7 were also analyzed. From Figure 15 it can be

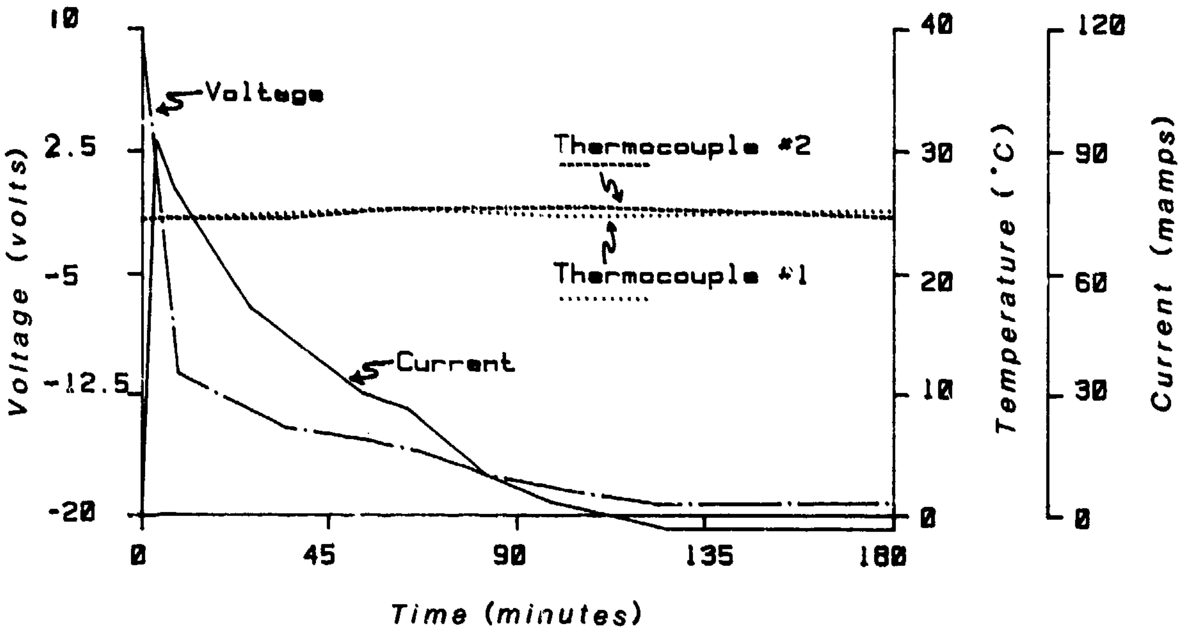

FIGURE 15. RESULTS OF FORCE OVERDISCHARGING AN SSXSV BATTERY (POTTED IN PROBE 7) AT THE C/2 RATE

seen that the voltage and current monitored on probe 7 dropped very rapidly unlike other discharges into voltage reversal. The temperatures monitored on probes 6 and 7 were on the outside of the canister which explains their ambient readings throughout testing.

Table 1 lists the contents of each gas collection vessel sent to the National Bureau of Standards. The report received from the Bureau indicated that no harmful or toxic gases were detected. Hydrogen gas (H_2) was detected in small quantities and therefore the possibility of a minor explosion exists. This could occur if the probes were exposed to temperatures exceeding roughly 200°C.

TABLE 1. ANALYSIS OF THE OFF-GAS PRODUCTS OF TWO Li/MnO_2 BATTERIES

Component	Composition, mole percent	
	Serial # 13978	Serial # 13979
H_2	4.1	11
CH_4	0.5	6.8
N_2	58	53
O_2	23	13
Ar	0.6	0.8
CO_2	13	7.8
CO	---	6.8
*HC	0.2	1.6

*Consists of one or more hydrocarbon constituents.

CHAPTER 4

CONCLUSIONS

The Duracell Li/MnO_2 DL$\frac{1}{3}$N cell and PX28L battery behaved well under abusive testing conditions characteristic of NAVSEA Notice 9310. The SSXSV battery made of one DL$\frac{1}{3}$N and one PX28L connected in series was found to be safe for use in the SSXSV probe. The probe configuration in which the DL$\frac{1}{3}$N and PX28L are completely potted does not allow for thermal expansion. Therefore, probes subjected to abusive conditions can be expected to crack. However, cracking does not lead to a safety problem. Using three DL$\frac{1}{3}$N cells connected in series with space for expansions or packing the cells in soft potting, would possibly improve probe durability. Mass spectrometric analysis of off-gas products (produced by battery abuse) did not detect harmful amounts of toxic gases. Small amounts of H_2 found in the venting products indicates the need to protect canister units from temperatures in excess of 200°C. However, the canister construction is durable enough to contain ventings of the SSXSV battery. Because of the ability of the canister to totally contain battery ventings, the SSXSV system is acceptable for internal carriage on a submarine.

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